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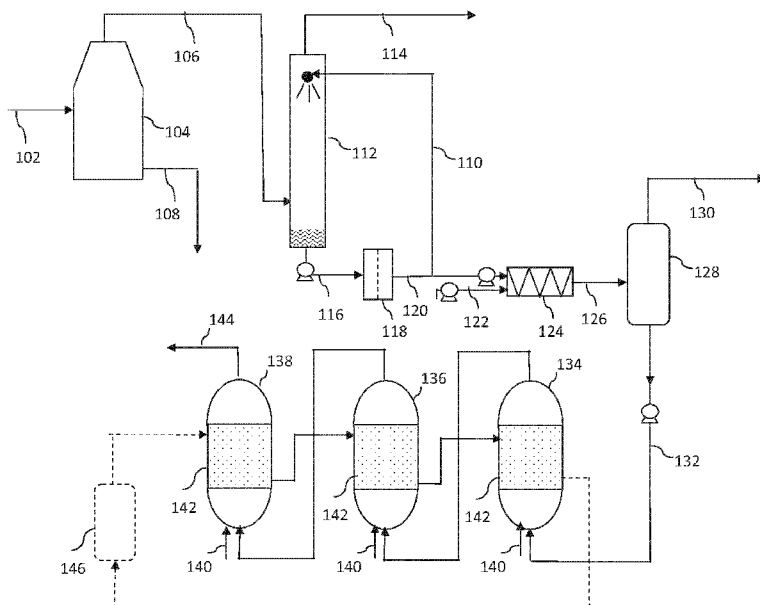
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(54) Title: PROCESS FOR CONVERTING A BIOMASS MATERIAL

Figure 1



(57) Abstract: A process for converting a biomass material comprising a) pyrolyzing a biomass material to produce a biomass-derived pyrolysis product; b) mixing at least part of the biomass-derived pyrolysis product and a petroleum-derived hydrocarbon composition, which petroleum derived hydrocarbon composition has a C7-asphaltenes content of equal to or more than 0.2 wt%, based on the total weight of the petroleum-derived hydrocarbon composition, to produce a hydrocarbon-containing mixture; c) dewatering the hydrocarbon-containing mixture to produce a dewatered hydrocarbon-containing mixture; d) contacting the dewatered hydrocarbon-containing mixture with hydrogen in one or more ebullating bed reactors comprising a catalyst at a temperature in the range from 350 to 500°C to produce a reaction product.

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PROCESS FOR CONVERTING A BIOMASS MATERIAL

Technical field of the invention

5 The present invention relates to a process for
converting a biomass material. More specifically the
present invention relates to a process for converting a
biomass material in a reaction product comprising one or
more cracked products. In addition the present invention
relates to a process for the preparation of biofuel
10 and/or biochemical.

Background to the invention

With the diminishing supply of crude petroleum oil,
use of renewable energy sources is becoming increasingly
important for the production of liquid fuels and/or
15 chemicals. The use of renewable energy sources may also
allow for a more sustainable production of liquid fuels
and more sustainable CO₂ emissions that may help meet
global CO₂ emissions standards under the Kyoto protocol.

The fuels and/or chemicals from renewable energy
20 sources are often referred to as biofuels and/or
biochemicals. Biofuels and/or biochemicals derived from
non-edible renewable energy sources, such as cellulosic
materials, are preferred as these do not compete with
food production. These biofuels and/or biochemicals are
25 also referred to as second generation, renewable or
advanced, biofuels and/or biochemicals. Most of these
non-edible renewable energy sources, however, are solid
materials that are cumbersome to convert into liquid
fuels.

30 For example US2011/0167713 describes a process for
direct hydroliquefaction of biomass. In this process a
suspension of particles of biomass in a solvent is
hydroconverted in two successive ebullating bed

reactors under hydrogen pressure to produce a fuel base. At least part of the fuel base produced in such process may undergo hydrocracking to improve the fuel base further. Such a process however, requires large amounts of hydrogen. In addition, energy is consumed by the suggested recycling of product. This makes the process of US2011/0167713 economically less attractive for scale up and/or commercial application.

US 2012/0004479 describes a method for making a diesel fuel product, comprising contacting a feedstock with a hydrotreating catalyst in a plurality of hydrotreating stages. In passing it is mentioned that the feedstock can include a pyrolysis oil. Furthermore it is mentioned in passing that at least a portion of one or more catalyst beds and/or stages can include an additional type of catalyst, such as a hydrocracking catalyst.

However, upgrading of pyrolysis oil in refinery equipment can be cumbersome due to its high water content, the presence of organic acids, and incompatibility with hydrocarbon liquids. At present, the upgrading of pyrolysis oil in refinery equipment requires retrofitting to prevent corrosion and fouling.

It would be an advancement in the art to provide a process that would allow one to convert biomass-derived pyrolysis oil in a safe and reliable manner through a refinery unit such as a hydrocracker to produce a product that has comparable characteristics as a conventional hydrocracker product, making it possible to process such biomass-derived pyrolysis oil in existing refineries.

Non-prepublished international patent application PCT/EP2012/071607 describes a method comprising upgrading

of a pyrolysis oil, which method comprises evaporating water from a mixture comprising the pyrolysis oil and a high boiling hydrocarbon (having an initial boiling point of at least 130°C at a pressure of 100 kiloPascal).

5 The pyrolysis oil is suitably obtained or derived from biomass comprising lignocellulosic material. The de-watered pyrolysis oil mixture may be used as a feedstock for hydrocarbon conversion processes. As an example of such a hydrocarbon conversion process, in passing,
10 hydrocracking is mentioned. As further explained in non-prepublished international patent application PCT/EP2012/071607 in a preferred embodiment the high boiling hydrocarbon or a mixture of high boiling hydrocarbons has an asphaltenes content of equal to or
15 more than 0.2 wt%, still more preferably equal to or more than 2.0 wt%.

A disadvantage, however, of using a high boiling hydrocarbon with a high asphaltenes content as described above is that a high boiling mixture with a high
20 asphaltenes content may obtained that may be difficult to process further.

It would be an advancement in the art to provide a process that allows one to further process such a high boiling mixture with a high asphaltenes content obtained
25 by a process as described in non-prepublished international patent application PCT/EP2012/071607, in a reliable and safe manner.

Summary of the invention

It has now been found that a high boiling mixture
30 with a high asphaltenes content, obtained by a process as described in non-prepublished international patent application PCT/EP2012/071607, can be advantageously further processed in a reliable and safe manner by

cracking it in one or more ebullating bed reactors, for example comprising a hydrocracking catalyst.

Accordingly the present invention provides a process for converting a biomass material comprising

- 5 a) pyrolyzing a biomass material to produce a biomass-derived pyrolysis product;
- b) mixing at least part of the biomass-derived pyrolysis product and a petroleum-derived hydrocarbon composition, which petroleum derived hydrocarbon composition has a C7-
10 asphaltenes content of equal to or more than 0.2 wt%, based on the total weight of the petroleum-derived hydrocarbon composition, to produce a hydrocarbon-containing mixture;
- c) dewatering the hydrocarbon-containing mixture to
15 produce a dewatered hydrocarbon-containing mixture;
- d) contacting the dewatered hydrocarbon-containing mixture with hydrogen in one or more ebullating bed reactors comprising a catalyst at a temperature in the range from 350 to 500°C to produce a reaction product.

20 The process according to the invention advantageously allows one to operate in an economically attractive, reliable and safe manner.

As indicated above, upgrading a biomass-derived pyrolysis product in refinery equipment, such as for
25 example a hydrocracker, can be cumbersome due to its high water content, the presence of organic acids, and incompatibility with petroleum-derived hydrocarbon compositions. For example, upgrading of a biomass-derived pyrolysis product containing water in a fixed bed reactor
30 at high temperatures may lead to a sudden formation of large amounts of steam, resulting in a so-called steam explosion. The removal of water from biomass-derived pyrolysis oil would improve the caloric value of biomass-

derived pyrolysis oil; would improve the compatibility with petroleum-derived hydrocarbon compositions; and would improve safety when operating in a fixed bed. However, the removal of water from a biomass-derived pyrolysis product by evaporation has led to undesirable results, such as the formation of a highly viscous, tar like material, which cannot be dissolved in a petroleum-derived hydrocarbon composition. In the process according to the invention, such problems can be avoided by mixing at least part of the biomass-derived pyrolysis product first with a petroleum-derived hydrocarbon composition to form a mixture and thereafter dewatering this mixture. It was found that evaporation of water from such a mixture does not lead to formation of highly viscous, tar like material or even solid material.

As illustrated in table III of non-prepublished international patent application PCT/EP2012/071607, however, depending on the percentage of biomass-derived pyrolysis product in the mixture, a higher C7-asphaltene content may be desired in order to obtain a stable mixture without solids formation after the dewatering step.

It has now been found that such a mixture having a high C7-asphaltene content may most conveniently be processed in the presence of hydrogen in one or more ebullating beds comprising a catalyst.

Conversion of the mixture in one or more fixed catalyst beds may lead to increased plugging of the catalyst beds, increasing the frequency of maintenance stops. In addition conversion of the mixture in one or more fixed catalyst beds may lead to an unstable or unsafe process if phase separation occurs after the mixture has become unstable.

Conversion of the mixture in one or more ebullating beds comprising a catalyst in the presence hydrogen may advantageously avoid the occurrence of such problems.

Brief description of the drawings

5 The invention has been illustrated by the following non-limiting figure:

Figure 1 illustrating an example of a process according to the invention.

Detailed description of the invention

10 In step a) of the process according to the invention a biomass material is pyrolyzed to produce a biomass-derived pyrolysis product.

By biomass material is herein understood a composition of matter of biological origin as opposed to a composition of matter obtained or derived from petroleum, natural gas or coal. Without wishing to be bound by any kind of theory it is believed that such biomass material may contain carbon-14 isotope in an abundance of about 0.0000000001 %, based on total moles of carbon.

20 The biomass material may suitably comprise animal fat, tallow and/or solid biomass material.

Preferably the biomass material is a solid biomass material. More preferably the biomass material is material containing cellulose and/or lignocellulose. Such a material containing "cellulose" respectively "lignocellulose" is herein also referred to as a "cellulosic", respectively "lignocellulosic" material. By a cellulosic material is herein understood a material containing cellulose and optionally also lignin and/or hemicellulose. By a lignocellulosic material is herein understood a material containing cellulose and lignin and optionally hemicellulose.

30 Examples of biomass materials include aquatic plants and algae, agricultural waste and/or forestry waste

and/or paper waste and/or plant material obtained from domestic waste. Examples of cellulosic or lignocellulosic material include for example agricultural wastes such as corn stover, soybean stover, corn cobs, rice straw, rice hulls, oat hulls, corn fibre, cereal straws such as wheat, barley, rye and oat straw; grasses; forestry products and/or forestry residues such as wood and wood-related materials such as sawdust and bark; waste paper; sugar processing residues such as bagasse and beet pulp; or mixtures thereof.

More preferably the solid biomass material comprises or consists of a cellulosic or lignocellulosic material selected from the group consisting of wood, sawdust, bark, straw, hay, grasses, bagasse, corn stover and/or mixtures thereof. The wood may include soft wood and/or hard wood.

When the biomass material is a solid biomass material such as for example a lignocellulosic material, it may suitably be washed, steam exploded, dried, roasted, torrefied and/or reduced in particle size before being pyrolyzed in step a). In addition, if the biomass material is a cellulosic or lignocellulosic material it may preferably be demineralized before being pyrolyzed in step a). During such a demineralization amongst others chloride may be removed.

In step a) the biomass material is pyrolyzed to produce a biomass-derived pyrolysis product. By pyrolysis or pyrolyzing is herein understood the decomposition of the biomass material, in the presence or in the essential absence of a catalyst, at a temperature of equal to or more than 380°C.

Preferably pyrolysis is carried out in an oxygen-poor, preferably an oxygen-free, atmosphere. By an

oxygen-poor atmosphere is understood an atmosphere containing equal to or less than 10 vol.% oxygen, preferably equal to or less than 5 vol.% oxygen and more preferably equal to or less than 1 vol.% oxygen. By an
5 oxygen-free atmosphere is understood an atmosphere where oxygen is essentially absent. More preferably pyrolysis is carried out in an atmosphere containing equal to or less than 2 vol.% oxygen, more preferably equal to or less than 0.5 vol.% oxygen, even more preferably equal to
10 or less than 0.1 vol. % oxygen and most preferably equal to or less than 0.05 vol.% oxygen. In a most preferred embodiment pyrolysis is carried out in the essential absence of oxygen.

The biomass material is preferably pyrolyzed at a
15 pyrolysis temperature of equal to or more than 400°C, more preferably equal to or more than 450°C, even more preferably equal to or more than 500°C and most preferably equal to or more than 550°C. The pyrolysis temperature is further preferably equal to or less than
20 800°C, more preferably equal to or less than 700°C and most preferably equal to or less than 650°C.

The pyrolysis pressure may vary widely. For practical purposes a pressure in the range from 0.01 to 0.5 MPa (MegaPascal), more preferably in the range from
25 0.1 to 0.2 MPa is preferred. Most preferred is an atmospheric pressure (about 0.1 MPa).

In one embodiment the pyrolysis does not include an externally added catalyst. In another embodiment the pyrolysis is a so-called catalytic pyrolysis wherein a
30 catalyst is used. Examples of suitable catalysts in such a catalytic pyrolysis include mesoporous zeolites. By a mesoporous zeolite is herein preferably understood a zeolite containing pores with a pore diameter in the

range from 2 - 50 nanometer, in line with IUPAC notation (see for example Rouquerol et al. (1994).

"Recommendations for the characterization of porous solids (Technical Report)" *Pure & Appl. Chem* 66 (8):

5 1739-1758). Especially preferred catalysts for such a catalytic pyrolysis include ZSM-5 type zeolites, such as for example Zeolyst 5524G and 8014 and Albemarle UPV-2.

In certain embodiments, chemicals may be employed for a pretreatment of the biomass material, or catalysts
10 may be added to the pyrolysis mixture, cf. for example, H Wang et al., "Effect of acid, alkali, and steam explosion pretreatment on characteristics of bio-oil produced from pinewood", *Energy Fuels* (2011) 25, p. 3758 - 3764.

In a preferred pyrolysis process, generally referred
15 to as a flash pyrolysis process, the biomass is rapidly heated (for example within 3 seconds) in the essential absence of oxygen to a temperature in the range of from 400 °C to 600 °C and kept at that temperature for a short period of time (for example equal to or less than 3
20 seconds). Such flash pyrolysis processes are known, for example from A. Oasmaa et al, "Fast pyrolysis of Forestry Residue 1. Effect of extractives on phase separation of pyrolysis liquids", *Energy & Fuels*, volume 17, number 1, 2003, pages 1-12; and A. Oasmaa et al, Fast pyrolysis
25 bio-oils from wood and agricultural residues, *Energy & Fuels*, 2010, vol. 24, pages 1380-1388; US4876108; US5961786; and US5395455.

In another preferred pyrolysis process a solid heating medium is used, such as for example silica or
30 sand. The solid heating medium may for example be a fluidized solid heating medium provided in for example a fluidized bed or a riser reactor. In such a pyrolysis process the biomass material may be fluidized within the

fluidized solid heating medium and subsequently the biomass material may be pyrolysed with the heat provided by such fluidized solid heating medium. Hereafter any residual coke formed on the solid heating medium may be
5 burned off to regenerate the solid heating medium. The coke that is burned off may conveniently supply the heat needed to preheat the solid heating medium.

The pyrolyzing in step a) may be carried out in any type of pyrolysis reactor known to the person skilled in the art to be suitable for such pyrolysis process. In a
10 special embodiment the pyrolysis reactor comprises a so-called screw reactor, wherein the biomass material is continuously conveyed through the heated reactor by means of a screw. Such a reactor is sometimes also referred to
15 as an "Auger" reactor.

During such pyrolysis of the biomass material a biomass-derived pyrolysis product is produced. The biomass-derived pyrolysis product referred to in this invention will contain water. The biomass-derived
20 pyrolysis product may for example contain gas, solids (char), one or more oily phase(s), and water. Optionally part of the water may be present as a separate aqueous phase, whereas another part of the water may be contained within one or more oily phase(s) in a dispersed and/or
25 emulsified form.

Step a) preferably further comprises separating one or more oily phase(s) containing water from the biomass-derived pyrolysis product. Such one or more oily phase(s) containing water are herein also referred to as pyrolysis
30 oil or biomass-derived pyrolysis oil. The pyrolysis oil or biomass-derived pyrolysis oil referred to in this invention hence will still contain water, for example in a dispersed and/or emulsified form.

In a preferred embodiment the biomass-derived pyrolysis oil is separated from any other components (for example, gas, solids or any aqueous phase) of the biomass-derived pyrolysis product. The biomass-derived pyrolysis oil can be separated from the biomass-derived pyrolysis product by any method known by the skilled person to be suitable for that purpose. This includes conventional methods such as filtration, centrifugation, cyclone separation, extraction, membrane separation and/or phase separation.

Preferably such a separation is carried out at a temperature of equal to or less than 100°C and a pressure of about 0.1 MegaPascal.

Preferably the biomass-derived pyrolysis product is separated in a liquid/solid separation, gas/liquid separation and/or a gas/liquid/solid separation to separate liquid biomass-derived pyrolysis product from the remainder of the biomass-derived pyrolysis product.

In a suitable embodiment, any biomass-derived pyrolysis product (also referred to as pyrolysis product vapours) or a part thereof may be at least partly condensed, for example by cooling the biomass-derived pyrolysis product. As a result of such condensation a condensed liquid, any residual vapours and optionally solids (such as for example any solid heating medium) may be obtained. The condensation can be carried out in any manner known to be suitable therefore by the person skilled in the art. For example by means of heat-exchangers. Preferably a condensation is carried out by cooling the biomass-derived pyrolysis product or part thereof with pyrolysis oil, suitably in one or more condensers, preferably in a counter-current arrangement. Any condensed vapours of the biomass-derived pyrolysis

product may suitably be captured in such counter
currently flowing pyrolysis oil. The so-obtained liquid
biomass-derived pyrolysis product may contain entrained
solids, such as for example the solid heating medium,
5 that may suitably be removed by filtration thereafter.
The obtained liquid biomass-derived pyrolysis product
preferably may consist mostly or wholly of biomass-
derived pyrolysis oil. Conveniently at least part of the
liquid biomass-derived pyrolysis product, preferably
10 consisting of biomass-derived pyrolysis oil, obtained
after filtration is used to condense the biomass-derived
pyrolysis product gas or part thereof.

In one embodiment the part of the biomass-derived
pyrolysis product that is liquid, may comprise one or
15 more oily phase(s) and optionally an aqueous phase.

In another, preferred embodiment, however, the part
of the biomass-derived pyrolysis product that is liquid
may also consist of one or more oily phase(s) comprising
dispersed and/or emulsified water therein.

20 The oily phase(s) are herein referred to as
pyrolysis oil or biomass-derived pyrolysis oil. In the
process of the invention, if any aqueous phase is present
in the liquid biomass-derived pyrolysis product, such
aqueous phase may or may not be separated from the one or
25 more oily phases. If separated, the aqueous phase may be
separated from the biomass-derived pyrolysis oil in for
example a water/oil phase separation step. However, even
after such a water/oil phase separation step,
considerable amounts of emulsified or dispersed water may
30 still remain within the oily phase.

The biomass-derived pyrolysis oil in the process of
the invention may include for example carbohydrates,
olefins, paraffins, oxygenates and residual water. By an

oxygenate is herein understood a compound containing carbon, hydrogen and oxygen. The oxygenates may for example include aldehydes, carboxylic acids, ethers, esters, alkanols, phenols and ketones.

5 The biomass-derived pyrolysis oil, or mixture of biomass-derived pyrolysis oil and aqueous phase may suitably comprise water in an amount equal to or more than 0.1 wt%, preferably equal to or more than 1wt%, more preferably equal to or more than 2 wt%, even more preferably equal to or more than 5 wt%, still more preferably equal to or more than 10 wt% and most preferably equal to or more than 15wt% water and preferably equal to or less than 55wt%, more preferably equal to or less than 45 wt%, and still more preferably equal to or less than 35 wt%, still more preferably equal to or less than 30 wt%, most preferably equal to or less than 25 wt%, based on the total weight of the biomass-derived pyrolysis oil, respectively the total weight of biomass-derived pyrolysis oil and aqueous phase. In practice, the biomass-derived pyrolysis oil or mixture of biomass-derived pyrolysis oil and aqueous phase may suitably comprise in the range from 1 to 55 wt%, more suitably in the range from 10 to 45 wt%, most suitably in the range from 15 to 35 wt%, based on the total weight of the biomass-derived pyrolysis oil, respectively the total weight of biomass-derived pyrolysis oil and aqueous phase.

 Preferably, the Total Acid Number of the biomass-derived pyrolysis oil may be at most 250 mg KOH/g, more preferably in the range of from 1 mg KOH/g to 200 mg KOH/g, even more preferably in the range of from 5 mg KOH/g to 150 mg KOH/g, most preferably in the range of from 10 mg KOH/g to 100 mg KOH/g.

As used herein, water content is as measured by ASTM E203 and Total acid number is as measured by using ASTM D664.

5 In addition, step a) may comprise demineralizing the biomass-derived pyrolysis product or part thereof (such as the biomass-derived pyrolysis oil), for example before forwarding to step b). During such a demineralization amongst others chloride may be removed. In a preferred embodiment, step a) may therefore further comprise the
10 removal of minerals such as chloride from the biomass material before pyrolyzing and/or the removal of minerals such as chloride from the biomass-derived pyrolysis product after pyrolyzing.

The biomass-derived pyrolysis product obtained in
15 step a) or part thereof may be forwarded directly or indirectly to step b). Preferably a biomass-derived pyrolysis oil is forwarded directly or indirectly to step b). For example the biomass-derived pyrolysis product or part thereof (such as the biomass-derived pyrolysis oil)
20 may first be stored for a period "t" before forwarding. Such a period "t" may preferably lie in the range from 1 hour to 1 month. The process according to the invention conveniently allows one to apply a method wherein:

- a biomass material is pyrolyzed to produce a
25 biomass-derived pyrolysis product, preferably a biomass-derived pyrolysis oil, in a location A;

- the produced biomass derived pyrolysis product or biomass-derived pyrolysis oil is optionally temporarily stored in a storage vessel and subsequently transported
30 to a location B;

- at least part of the biomass-derived pyrolysis product, or preferably the biomass-derived pyrolysis oil, is mixed with a petroleum-derived hydrocarbon composition

in location B, whereafter the obtained mixture is dewatered in location B.

In step b) of the process according to the invention, at least part of the biomass-derived pyrolysis product is mixed with a petroleum-derived hydrocarbon composition, which petroleum derived hydrocarbon composition has a C7-asphaltenes content of equal to or more than 0.2 wt%, based on the total weight of the petroleum-derived hydrocarbon composition, to produce a hydrocarbon-containing mixture.

In a preferred embodiment the "at least part of the biomass-derived pyrolysis product" comprises or consists of that part of the pyrolysis product that is liquid at a temperature of for example 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C or 100°C and a pressure of 0.1 MegaPascal. More preferably the "at least part of the biomass-derived pyrolysis product" comprises or consists of a biomass-derived pyrolysis oil as described above, i.e. a biomass-derived pyrolysis oil comprising for example dispersed and/or emulsified water therein. If applicable, the part of the pyrolysis product provided in step b) may conveniently be separated from the pyrolysis product by any of the methods such as filtration, centrifugation, cyclone separation, extraction, membrane separation and/or phase separation as mentioned above.

The petroleum-derived hydrocarbon composition may comprise one or more hydrocarbon compounds and preferably comprises two or more hydrocarbon compounds. By a hydrocarbon compound is herein understood a compound containing hydrogen and carbon. Such hydrocarbon compound may further contain heteroatoms such as oxygen, sulphur and/or nitrogen. The petroleum-derived hydrocarbon

composition may also comprise hydrocarbon compounds consisting of only hydrogen and carbon.

In a preferred embodiment, the C7-asphaltenes content of the petroleum-derived hydrocarbon composition may be equal to or more than 0.2 %wt (percent by weight), more preferably equal to or more than 0.7 %wt, still more preferably equal to or more than 2.0 %wt, even more preferably in the range of from 0.8 to 30 %wt, still even more preferably in the range of from 2.0 %wt to 30 %wt, based on the total weight of the petroleum-derived hydrocarbon composition. Most preferably the C7-asphaltenes content is in the range of from 0.9 to 15 %wt or in the range of from 2.0 to 15 %wt based on the total weight of the petroleum-derived hydrocarbon composition. As used herein, asphaltene content or C7-asphaltene content is as determined by IP143, using n-heptane as a solvent.

Suitable the petroleum-derived hydrocarbon composition has an initial atmospheric boiling point of equal to or more than 130 °C. Preferably, the initial atmospheric boiling point of the petroleum-derived hydrocarbon composition is equal to or more than 150 °C, more preferably equal to or more than 180 °C. In preferred embodiments, the atmospheric boiling point range of the petroleum-derived hydrocarbon composition may be from 220 °C to 800 °C, more preferably from 300 °C to 700 °C. In preferred embodiments, the hydrogen to carbon weight ratio (H/C ratio) of the petroleum-derived hydrocarbon composition may be at most 0.15 w/w, more preferably in the range of from 0.1 to 0.14 w/w, even more preferably in the range of from 0.11 to 0.13 w/w.

As used herein, boiling point is the atmospheric boiling point, unless indicated otherwise, with the

atmospheric boiling point being the boiling point as determined at a pressure of 100 kiloPascal (i.e. 0.1 MegaPascal). As used herein, initial boiling point and boiling point range of the high boiling hydrocarbon mixtures are as determined by ASTM D2887. As used herein, pressure is absolute pressure. As used herein, H/C ratio is as determined by ASTM D5291. As used herein, asphaltenes content or C7-asphaltenes content is as determined by IP143, using n-heptane as a solvent.

In a preferred embodiment the petroleum-derived hydrocarbon composition comprises shale oil, oil derived from oil sands, bitumen, a straight run (atmospheric) gas oil, a flashed distillate, a vacuum gas oil (VGO), a coker (heavy) gas oil, a diesel, a gasoline, a kerosene, a naphtha, a liquefied petroleum gas, an atmospheric residue ("long residue"), a vacuum residue ("short residue") and/or mixtures thereof. Most preferably the petroleum-derived hydrocarbon composition comprises an atmospheric residue or a vacuum residue. The petroleum-derived hydrocarbon composition may suitably also be derived from an unconventional oil resource such as oil shale or oil sands. For example the petroleum-derived hydrocarbon composition may comprise a pyrolysis oil derived from oil shale or oil sands.

The mixture of the biomass-derived pyrolysis product or part thereof (for example the biomass-derived pyrolysis oil) and the petroleum-derived hydrocarbon composition can be produced in any manner known to the skilled person in the art. The part or whole of the biomass-derived pyrolysis product may be added to the petroleum-derived hydrocarbon composition, or the petroleum-derived hydrocarbon composition may be added to part or whole of the biomass-derived pyrolysis product,

or streams of for example the biomass-derived pyrolysis product or part thereof and the petroleum-derived hydrocarbon composition may be brought together, for example by in-line blending. Suitably the part or whole of the biomass-derived pyrolysis product and the petroleum-derived hydrocarbon composition may be mixed, for example in an in-line mixer or static mixer. Preferably the part or whole of the biomass-derived pyrolysis product is a biomass-derived pyrolysis oil as described herein above.

Preferably, the biomass-derived pyrolysis oil and the petroleum-derived hydrocarbon composition may be mixed in a weight ratio of biomass-derived pyrolysis oil to petroleum-derived hydrocarbon composition (grams biomass-derived pyrolysis oil/grams petroleum-derived hydrocarbon composition) of at least 0.5/99.5, more preferably at least 1/99, still more preferably at least 2/98, and even still more preferably at least 5/95, respectively. Preferably, the biomass-derived pyrolysis oil and the petroleum-derived hydrocarbon composition may be mixed in a weight ratio of biomass-derived pyrolysis oil to petroleum-derived hydrocarbon composition (grams biomass-derived pyrolysis oil/grams petroleum-derived hydrocarbon composition) of at most 75/25, more preferably at most 70/30, even more preferably at most 60/40, and most preferably at most 50/50 respectively. In an especially preferred embodiment the petroleum-derived hydrocarbon composition may be mixed in a weight ratio of biomass-derived pyrolysis oil to petroleum-derived hydrocarbon composition (grams biomass-derived pyrolysis oil/grams petroleum-derived hydrocarbon composition) in the range from 1/99 to 30/70, more preferably in the

range from 5/95 to 25/75, most preferably in the range from 10/90 to 20/80.

In a preferred embodiment the amount of biomass-derived pyrolysis oil in a mixture comprising a biomass-derived pyrolysis oil and a petroleum-derived hydrocarbon composition, varies depending on the asphaltene content of the petroleum-derived hydrocarbon composition. This may allow for an optimal stability of the mixture comprising the biomass-derived pyrolysis oil and the petroleum-derived hydrocarbon composition. For example, when a petroleum-derived hydrocarbon composition is used comprising equal to or less than 0.2 wt% of asphaltenes, the weight ratio of biomass-derived pyrolysis oil to petroleum-derived hydrocarbon composition (grams biomass-derived pyrolysis oil/grams petroleum-derived hydrocarbon composition) is preferably equal to or less than 10/90, more preferably in the range from equal to or more than 0.5/99.5 to equal to or less than 10/90. When a petroleum-derived hydrocarbon composition is used comprising in the range from more than 0.2 wt% to equal to or less than 0.5wt% of asphaltenes, the weight ratio of biomass-derived pyrolysis oil to petroleum-derived hydrocarbon composition (grams biomass-derived pyrolysis oil/grams petroleum-derived hydrocarbon composition) is preferably equal to or less than 15/85, more preferably in the range from equal to or more than 0.5/99.5 to equal to or less than 15/85. When a petroleum-derived hydrocarbon composition is used comprising in the range from more than 0.5 wt% to equal to or less than 1.3 wt% of asphaltenes, the weight ratio of biomass-derived pyrolysis oil to petroleum-derived hydrocarbon composition (grams biomass-derived pyrolysis oil/grams petroleum-derived hydrocarbon composition) is preferably

equal to or less than 20/80, more preferably in the range from equal to or more than 0.5/99.5 to equal to or less than 20/80. When a petroleum-derived hydrocarbon composition is used comprising in the range from more than 1.3 wt% to equal to or less than 2.3 wt% of asphaltenes, the weight ratio of biomass-derived pyrolysis oil to petroleum-derived hydrocarbon composition (grams biomass-derived pyrolysis oil/grams petroleum-derived hydrocarbon composition) is preferably equal to or less than 30/70, more preferably in the range from equal to or more than 0.5/99.5 to equal to or less than 30/70. When a petroleum-derived hydrocarbon composition is used comprising more than 2.3 wt% of asphaltenes, the weight ratio of biomass-derived pyrolysis oil to petroleum-derived hydrocarbon composition (grams biomass-derived pyrolysis oil/grams petroleum-derived hydrocarbon composition) is preferably equal to or less than 60/40, more preferably in the range from equal to or more than 0.5/99.5 to equal to or less than 60/40.

The biomass-derived pyrolysis oil and the petroleum-derived hydrocarbon composition can be mixed in any manner known by the skilled in the art to be suitably for mixing, for example by means of a mixer or via one or more baffles.

Step b) results in a hydrocarbon-containing mixture being produced. This hydrocarbon-containing mixture produced in step b) will still contain water, for example in a dispersed or emulsified form.

In step c) of the process according to the present invention the hydrocarbon-containing mixture is dewatered to produce a dewatered hydrocarbon-containing mixture.

During such dewatering, water is suitably removed from the water-containing hydrocarbon-containing mixture.

Dewatering can be carried out in any manner known by the person skilled in the art to be suitable for the removal of water from a hydrocarbon-containing mixture containing water.

Dewatering of the hydrocarbon-containing mixture may for example be carried out by evaporating of the water; membrane separation; phase separation; absorption or adsorption of the water; and/or any combination thereof. The dewatering may be carried out in a continuous operation or as a batch operation.

Preferably the hydrocarbon-containing mixture is dewatered by means of evaporation. Evaporation of the water, and optionally any volatile acids, from the hydrocarbon-containing mixture may for example be achieved by flashing or distillation of the hydrocarbon-containing mixture. In another example the water may be evaporated from the hydrocarbon-containing mixture in one or more wipe-film evaporators connected in series.

In a preferred embodiment water, and optionally any volatile acids, are evaporated from the hydrocarbon-containing mixture by flashing of such hydrocarbon-containing mixture. The flashing may for example be carried out by feeding a hydrocarbon-containing mixture under a pressure for example in the range from 200 to 1000 KiloPascal (KPa) into a flash vessel operated at a pressure for example in the range from 0.1 to 50 KPa at for example a temperature in the range from 90 to 150°C.

In another embodiment a distillation apparatus having a separation column may be selected to evaporate the water. The separation column may preferably be selected and operated such that it comprises at most

fifty (inclusive), more preferably at most forty (inclusive), in particular at most thirty (inclusive) theoretical trays. Preferably, the separation column may preferably be selected and operated such that it
5 comprises at most ten (inclusive) or at most five (inclusive) theoretical trays.

Preferably, the distillation apparatus and the conditions of operating the distillation apparatus are selected such that water is evaporated and condensed as a
10 water rich distillate fraction, and higher boiling hydrocarbon compounds (for example hydrocarbon compounds boiling at a temperature of equal to or more than 100°C, preferably at a temperature of equal to or more than
130°C, more preferably at a temperature of equal to or
15 more than 150°C and most preferably at a temperature of equal to or more than 180°C at a pressure of 0.1 MegaPascal) remains in the bottom, yielding a bottom fraction which is rich in such higher boiling hydrocarbon compounds.

20 Preferably the bottom temperature is selected such that the bottom fraction is sufficiently low in viscosity, and the rate of evaporation of water is sufficiently high at the prevailing pressure and remains sufficiently high at instances that the water content of
25 the bottom fraction is low. Suitably, a bottom temperature in the range of from 50 °C to 200 °C may be selected, more suitable in the range of from 80 °C to 150 °C. The pressure may suitably be selected in the range of from 0.01 kPa to 500 kPa, more suitably in the
30 range of from 0.1 kPa to 120 kPa, preferably in the range of from 0.2 kPa to 60 kPa and more preferably in the range of from 0.2 kPa to 10 kPa (kiloPascal). Although the higher boiling hydrocarbon compounds have been

defined hereinbefore by its atmospheric boiling point (i.e. at a pressure of 0.1 MegaPascal, the skilled person will appreciate that the atmospheric boiling point is specified such that a distillation apparatus can be
5 operated at a pressure other than atmospheric pressure (i.e. 0.1 MegaPascal) while water is evaporated and condensed as a water rich distillate fraction, and higher boiling hydrocarbon compounds remain in the bottom, yielding a bottom fraction which is rich in the higher
10 boiling hydrocarbon compounds. Such bottom fraction can suitably be used as a dewatered hydrocarbon-containing mixture, in the next steps of the process according to this invention.

In step c) preferably equal to or more than 1 wt% of
15 the total weight of water in the hydrocarbon-containing mixture is removed, more preferably equal to or more than 10 wt%, even more preferably equal to or more than 50wt%, still more preferably equal to or more than 70wt% and most preferably equal to or more than 90 wt% of the total
20 weight of water in the hydrocarbon-containing mixture is removed. Suitably equal to or less than 100 wt% of the total weight of water in the hydrocarbon-containing mixture can be removed.

Dewatering of the hydrocarbon-containing mixture may
25 preferably be effected to the extent that a dewatered hydrocarbon-containing mixture is obtained. The dewatered hydrocarbon-containing mixture preferably has a water content of at most 5 %wt, more preferably at most 2 %wt, preferably at most 1 %wt, based on the total weight of
30 the dewatered hydrocarbon-containing mixture. In the normal practice of this invention the water content of the dewatered hydrocarbon-containing mixture obtained may be at least 0.001 %wt, or at least 0.01 %wt, based on the

total weight of the dewatered hydrocarbon-containing mixture.

The dewatered hydrocarbon-containing mixture obtained in step c) or part thereof may be forwarded directly or indirectly to step d). For example the dewatered hydrocarbon-containing mixture obtained in step c) or part thereof may first be stored for a period "t" before forwarding. Such a period "t" may preferably lie in the range from 1 hour to 1 month.

After dewatering step c) it is possible, if so desired, to add a further petroleum-derived hydrocarbon composition to the dewatered hydrocarbon-containing mixture. This further petroleum-derived hydrocarbon composition may be the same or different from the petroleum-derived hydrocarbon composition used in mixing step b).

In step d) of the process according to the invention, the dewatered hydrocarbon-containing mixture is contacted with hydrogen in one or more ebullating bed reactors comprising a catalyst at a temperature in the range from 350 to 500°C to produce a reaction product.

In one embodiment, step d) may comprise supplying a feed comprising the dewatered hydrocarbon-containing mixture together with one or more co-feeds to the one or more ebullating bed reactors and/or contacting the dewatered hydrocarbon-containing mixture with the catalyst in the presence of such one or more co-feeds. Such co-feeds may for example comprise one or more further petroleum-derived hydrocarbon compositions as described herein above. This further petroleum-derived hydrocarbon composition may be the same or different from the petroleum-derived hydrocarbon composition used in mixing step b).

Such co-feeds may, however, also comprise a lignocellulosic or cellulosic material as described herein above for step (a) or a so-called biocrude obtained by liquefaction of such a lignocellulosic or cellulosic material. When the co-feed comprises such lignocellulosic or cellulosic material, such lignocellulosic or cellulosic material may conveniently be liquefied during step d). Alternatively, a lignocellulosic or cellulosic material may be converted in a first fixed or ebullated bed reactor in the presence of a catalyst and optionally hydrogen at a temperature equal to or less than 350°C to produce a biocrude, whereafter such a biocrude is supplied as a co-feed to step d).

The process according to the invention therefore conveniently also provides a process comprising:

- a) pyrolyzing a biomass material to produce a biomass-derived pyrolysis product;
- b) mixing at least part of the biomass-derived pyrolysis product and a petroleum-derived hydrocarbon composition, which petroleum derived hydrocarbon composition has a C7-asphaltenes content of equal to or more than 0.2 wt%, based on the total weight of the petroleum-derived hydrocarbon composition, to produce a hydrocarbon-containing mixture;
- c) dewatering the hydrocarbon-containing mixture to produce a dewatered hydrocarbon-containing mixture; wherein a feed comprising the dewatered hydrocarbon-containing mixture is co-fed with a co-feed comprising a petroleum-derived hydrocarbon composition and/or a lignocellulosic material and/or a cellulosic material to one or more ebullating bed reactors comprising a catalyst and converted therein to produce a reaction product.

Preferably the conversion in one or more of the ebullating bed reactors is carried out in the presence of hydrogen. In addition, the temperature in one or more of the ebullating bed reactors is preferably the range from 350 to 500°C. The reaction product preferably comprises one or more cracked products as described herein.

Step d) is preferably carried out at a temperature in the range from equal to or more than 350°C to equal to or less than 470°C, more preferably in the range from equal to or more than 370°C to equal to or less than 450°C, most preferably in the range from equal to or more than 390°C to equal to or less than 435°C.

Step d) is preferably carried out at a total pressure in the range from equal to or more than 1 MegaPascal (MPa) to equal to or less than 30 MPa, more preferably in the range from equal to or more than 5 MPa to equal to or less than 25 MPa, most preferably in the range from equal to or more than 8 MPa to equal to or less than 20 MPa.

The hydrogen in step d) is preferably provided as a hydrogen gas. The quantity of hydrogen contacted with the dewatered hydrocarbon-containing mixture preferably lies in the range from 0.1 to 2 normal cubic meters (Nm³) per kg of dewatered hydrocarbon-containing mixture. In a preferred embodiment the hydrogen gas is provided in a partial pressure that is in the range from 50% to 99%, more preferably in the range from 60% to 95%, still more preferably in the range from 70% to 90%, most preferably in the range from 80% to 90% of the total pressure.

The dewatered hydrocarbon-containing mixture is contacted with hydrogen in one or more ebullating bed reactors comprising a catalyst. Preferably the one or more ebullating bed reactors comprise 2 or 3 ebullating bed reactors. Preferably the one or more ebullating bed

reactors are lined up in sequence, where conventionally the catalyst is forwarded through the ebullating bed reactors in a direction counter current to the direction of the dewatered hydrocarbon-containing mixture.

5 Instead of one or more ebullating bed reactors also one or more moving bed reactors and/or one or more slurry reactors, may be used. It is also possible to use a combination of ebullating bed reactors, moving bed reactors and/or slurry reactors. That is, step d) may be
10 carried out in one or more reactors where each reactor individually can be an ebullating bed reactor, a moving bed reactor or a slurry reactor. For example the one or more reactors may comprise or consist of one or more ebullating bed reactors and/or one or more slurry
15 reactors. Most preferably the one or more reactors are one or more ebullating bed reactors. In the process according to the invention, such one or more ebullated bed reactors may each conveniently comprise a liquid phase comprising the dewatered hydrocarbon-containing
20 mixture; a solid phase comprising one or more catalysts; and a gaseous phase comprising hydrogen gas.

 In step d) the dewatered hydrocarbon-containing mixture may preferably be hydrocracked. Step d) may therefore preferably be a hydrocracking step and the
25 reactors are preferably hydrocracking reactors. The catalyst used in step d) may preferably be a hydrocracking catalyst. The reaction product produced in step d) is preferably a reaction product comprising one or more cracked products.

30 The catalyst is preferably a catalyst comprising one or more metals of group VIII of the periodic table and/or one or more metals metal of group VIB of the periodic table. For example the catalyst may comprise a metal

selected from the group comprising nickel, palladium, molybdenum, tungsten, platinum, cobalt, rhenium and/or ruthenium. Most preferably the catalyst is a nickel/tungsten comprising catalyst, a nickel/molybdenum comprising catalyst, cobalt/tungsten comprising catalyst or cobalt/molybdenum comprising catalyst. Suitably the above mentioned metals may be present in an alloy or oxide form.

Preferably the catalyst further comprises a support, which may be used to carry the metal or metals. Such a catalyst comprising one or more metals on a support is herein also referred to as heterogeneous catalyst. Examples of suitable supports include alumina, silica, silica-alumina, zirconia, titania, and/or mixtures thereof. The support may comprise a zeolite, but preferably comprises amorphous alumina, silica or silica-alumina.

Most preferably the catalyst comprises one or more oxides of molybdenum, cobalt, nickel and/or tungsten on a carrier comprising amorphous alumina, silica or silica-alumina.

The catalyst may be prepared in any manner known to be suitable by the person skilled in the art. In a preferred embodiment, the catalyst is a so-called extruded catalyst, prepared by extrusion of its components.

In a preferred embodiment the catalyst is a sulfided catalyst. The catalyst may be sulfided in-situ or ex-situ.

In a preferred embodiment the catalyst is sulfided in-situ or its sulfidation is maintained in-situ by contacting it with a stream of hydrogen that comprises hydrogen sulfide, for example a stream of hydrogen that

contains in the range from 0.1 to 10wt% hydrogensulfide based on the total weight of the stream of hydrogen.

In addition to a heterogeneous catalyst or instead of a heterogeneous catalyst, also a colloidal or dispersed catalyst may be used. Conveniently such a colloidal or dispersed catalyst may be formed in-situ by mixing one or more catalyst precursors in the feed in such a manner that a colloidal or dispersed catalyst is formed within the one or more ebullating bed reactors.

In step d) preferably a reaction product is produced comprising one or more cracked products. By a cracked product is herein understood a product comprising one or more compounds obtained by cracking of one or more larger compounds.

In a preferred embodiment the reaction product or part thereof is subsequently fractionated to produce one or more product fractions. For example a product fraction boiling in the gasoline range (for example from about 35°C to about 210°C); a product fraction boiling in the diesel range (for example from about 210°C to about 370°C); a product fraction boiling in the vacuum gas oil range (for example from about 370°C to about 540°C); and a short residue product fraction (for example boiling above 540°C).

Any one or more product fractions obtained by fractionation may or may not be further hydrotreated or hydroisomerized to obtain a hydrotreated or hydroisomerized product fraction.

The, optionally hydrotreated or hydroisomerized, product fraction(s) may be used as biofuel and/or biochemical component(s).

In a preferred embodiment the, optionally hydrotreated or hydroisomerized, one or more product

fractions produced in the fractionation can be blended as a biofuel component and/or a biochemical component with one or more other components to produce a biofuel and/or a biochemical. By a biofuel respectively a biochemical is herein understood a fuel or a chemical that is at least 5 party derived from a renewable energy source.

Examples of one or more other components with which the, optionally hydrotreated or hydroisomerized, one or more product fractions may be blended include anti-oxidants, corrosion inhibitors, ashless detergents, 10 dehazers, dyes, lubricity improvers and/or mineral fuel components, but also conventional petroleum derived gasoline, diesel and/or kerosene fractions.

One of the embodiments according to the invention is 15 illustrated in figure 1. In figure 1 a feed (102) comprising a biomass material is supplied to a pyrolysis reactor (104). In the pyrolysis reactor (104) the biomass material is heated to a temperature of 500°C in the absence of oxygen to produce 20 a pyrolysis product (106). Solid char (108) remaining after the pyrolysis is removed via the bottom of pyrolysis reactor (104). The pyrolysis product (106) is cooled in a condenser (112) with a cooled stream of pyrolysis oil (110), allowing the pyrolysis product to be 25 separated into gaseous byproducts (114) and a cooled pyrolysis oil (116) comprising emulsified water and entrained solid particles. The cooled pyrolysis oil (116) comprising emulsified water and entrained solid particles is subsequently forwarded to a filter (118) allowing the 30 entrained solid particles to be filtered out. The filtered cooled pyrolysis oil (120) is partly recycled as cooled stream of pyrolysis oil (110) for the condenser (112). Another part of the filtered cooled pyrolysis oil

(120) is mixed with a long residue having a C7-
asphaltenes content of about 5 wt% (122) in a static
mixer (124) to produce a hydrocarbon-containing mixture
(126). The a hydrocarbon-containing mixture (126) is
5 dewatered in a flash vessel (128) operated at a
temperature of 120°C and a pressure of about 5 KPascal to
obtain a water stream (130) and a dewatered hydrocarbon
containing mixture (132). The dewatered hydrocarbon
containing mixture (132) is forwarded to a series of a
10 first hydrocracker (134), a second hydrocracker (136) and
a third hydrocracker (138), where the dewatered pyrolysis
oil (132) is contacted with a stream of hydrogen (140)
and a hydrocracker catalyst (142) to produce a reaction
product comprising one or more cracked products (144).
15 The hydrocracking catalyst of third hydrocracker reactor
(138) is conveniently reused subsequently in the second
hydrocracker (136) reactor and the third hydrocracker
reactor (134) in a sequence countercurrent to the feed of
dewatered hydrocarbon containing mixture (132). Hereafter
20 the hydrocracking catalyst can optionally be regenerated
in a regenerator (146).
The reaction product comprising one or more cracked
products (144) can conveniently be further processed in
one or more additional processing steps (such as for
25 example a fractionation, or further hydroprocessing
steps) to provide a fuel component (not shown).

Example 1

Pyrolysis oil was produced by pyrolysis of forest residue
at a temperature of about 500°C in an inert atmosphere.
30 The pyrolysis oil had a water content of about 23.9 wt%
as determined by Karl Fisher titration according to
ASTM6304, based on the total weight of the sample. The
elemental composition of the pyrolysis oil is summarized
in table 1 below.

Table 1: Composition of Pyrolysis Oil from Forest Residue.

C, %wt.	H, %wt.	N, %wt.	S, %wt.	O (**), %wt.	Basis
40.1	7.6	0.1	<0.00	52.2	Wet basis*
60.5	7.4	0.1	<0.00	32.0	Dry basis (calc. from wet basis***)

5 * C,H,N according to ASTM D5291 and S according to ASTM D2622

** Oxygen content calculated by difference, i.e. by subtracting carbon, hydrogen, nitrogen and sulphur content from 100 wt%.

10 *** Water content of about 23.9 wt% as determined by Karl Fisher titration according to ASTM6304 was subtracted from the total mass before calculation of the percentages on a dry basis.

15 A 12 kilogram (kg) mixture was prepared by mixing the above pyrolysis oil with a so-called Arabian Medium Vacuum Residue (a petroleum-derived hydrocarbon composition) in a weight ratio of pyrolysis oil to Arabian Medium Vacuum Residue of 5:95. Some characteristics of the Arabian Medium Vacuum Residue are provided in table 2.

20 The Arabian Medium Vacuum Residue was preheated to a temperature of about 80°C and conveyed to a vessel, whereafter a specific amount of pyrolysis oil was added such as to allow a mixture to be formed containing 5 wt% (weight%) of pyrolysis oil and 95 wt% of Arabian Medium Vacuum Residue.

25 Water was removed from the resulting mixture during about 2 hours by means of a rotating vacuum evaporator set at about 90°C at a pressure of about 25 mbar (2.5

KiloPascal (KPa)) to obtain a dewatered hydrocarbon-containing mixture. The water content of the dewatered hydrocarbon-containing mixture was analyzed by means of a Karl Fisher titration pursuant to ASTM D6304 to be about 5 0.13 wt%, based on the total weight of the mixture. Based on a 60 % yield during the water evaporating step, the dewatered hydrocarbon-containing mixture was estimated to contain around 3 %wt dewatered pyrolysis oil. Approximately 10 kg of this dewatered hydrocarbon- 10 containing mixture was sampled for example 2.

Table 2: Characteristics of Arabian Medium Vacuum Residue

Property	Method	Results
Density @ 60 °F (15.6 °C), kg/l	ASTM D - 70	1.0238
Micro Carbon Residue, %wt.	ASTM D - 4530	22.74
Nickel, ppmw.	ASTM D - 5863A	47
Vanadium, ppmw.	ASTM D - 5863A	124
Iron, ppmw.	ASTM D - 5863A	29
Toluene Insolubles, %wt.	ASTM D - 473	0.03
Viscosity @ 100 °C, cSt	ASTM D - 445	2153
Viscosity @ 149 °C, cSt	ASTM D - 445	229
Ash content, %wt.	ASTM D - 482	0.05
Water content, by distillation, %v/v.	ASTM D - 95	0.05
Saturates, %wt.	ASTM D - 4124	6.2
Naphthenic Aromatics, %wt.	ASTM D - 4124	41.4
Polar Aromatics, %wt.	ASTM D - 4124	39.7
Heptane Insolubles, %wt.	IP - 143	12.7
Total, %wt.	Sum of saturates, naphthenic aromatics, polar aromatics and heptanes insolubles	100
Pentane insolubles, %wt.	IP - 143M	18.9
Carbon content, %wt.	ASTM D - 5291	83.54
Hydrogen content, %wt.	ASTM D - 5291	10.12
Nitrogen, %wt	ASTM D - 5291	0.39
H/ C Atomic Ratio	(H%wt/C%wt)* atomic weight carbon (12)	1.45
Sulphur content, %wt.	ASTM D2622 (X-ray)	5.81
Chloride content, ppmw		<10
TAN, mg KOH/g	ASTM D - 664	0.25

Example 2:

5 Example 2 was carried out in a simulated two-stage ebullated bed unit that consisted of two continuous stirred tank reactor (CSTR) units connected together in series. Each CSTR unit consisted of a one liter autoclave equipped with a Robinson Mahoney catalyst basket. A flow

of hydrogen gas was added to a feed of dewatered hydrocarbon-containing mixture as prepared in example 1 prior to entering the first CSTR. Both liquid and gas flowed from the first CSTR unit to the second CSTR unit, with no interstage addition or withdrawal. The product was obtained from the second CSTR unit.

The operating conditions are summarized in table 3. The operating conditions were the same for both CSTR units.

In each CSTR unit, the combined flow of hydrogen gas and feed of dewatered hydrocarbon-containing mixture was contacted with a sulphided catalyst in the form of cylindrical extrudates having a diameter of about 1 mm containing 6 wt% molybdenum and 2.4 wt% nickel on a alumina carrier (the catalyst was commercially obtained from Criterion). The catalyst was loaded into the CSTR units in its oxide form, whereafter sulfidation of the catalyst was carried out in situ, with a heavy feed containing about 6wt% sulfur at a flow rate of 58.2 grams/hour a pressure of 15.5 MegaPascal (MPa) with a temperature ramp of 32°C per hour to 400°C followed by an overnight soak at 400°C.

Table 3: Operating Conditions

Condition	Value
Catalyst amount per reactor, (grams)	29.75
Liquid feed rate, (gram/hour)	67
H ₂ flow rate, (standard liters/hour)*	47.2
Total pressure (MPa)	15.5
Liquid temperature, °C	424
Overall catalyst based LHSV (hr ⁻¹) **	0.55

* standard liters/hour are determined at 20°C and 0.1 MPa.

** ml of feed/per hour/ per ml catalyst bed.

For example 2, a run was carried out containing three working periods as reflected in table 4. In the first working period (0 to 104 hours) a feed consisting only of Arabian Medium Vacuum Residue was contacted with the hydrogen and the catalyst; in the second working period (104-188 hours) a feed comprising the mixture as prepared in example 1 was contacted with the hydrogen and the catalyst; and in the third working period again a feed consisting only of Arabian Medium Vacuum Residue was contacted with the hydrogen and the catalyst. During the run, the catalyst was not refreshed.

Table 4: Overview of work periods and used feedstock.

Period 1 0 - 104 hours	Period 2 104 - 188 hours	Period 3 188 - 256 hours
Arabian Medium Vacuum Residue only	dewatered hydrocarbon-containing mixture as prepared in example 1	Arabian Medium Vacuum Residue only

During each of the working periods samples of the total liquid product (TLP) were collected. The total liquid product (TLP) samples were collected on the last day before a feed switch took place. This TLP was nitrogen stripped to remove any residual H₂S. The stripped TLP was subsequently analyzed for sulphur content, micro carbon residue (MCR) content and boiling point distribution.

The boiling fractions for the stripped TLP obtained with the feed containing only Arabian Medium Vacuum Residue (comparative); and for the stripped TLP obtained for the feed containing the dewatered hydrocarbon-containing mixture as prepared in example 1 (according to the invention) are listed in table 5. The components in

the fraction boiling below 370°C (i.e. the gasoline and diesel range fractions) were analyzed and are summarized in table 6. The components in the fraction boiling above 370°C (i.e. the vacuum gas oil and short residue range fractions) were analyzed and are summarized in table 7 (components with boiling up to 470 °C could be determined only).

The elemental composition of the stripped TLP for is summarized in tables 8, 9 and 10, this includes the sulphur content.

Further the Bio-carbon content was determined ASTM D6866 for the stripped TLP boiling fractions above and below 370°C obtained in the second working period. It was found that the Bio-carbon content in the feed (i.e. the dewaterd hydrocarbon containing mixture as prepared in example 1) was about 1.8 wt%, based on the total weight of the feed. The Bio-carbon content in the stripped TLP fraction boiling below 370°C was about 2.0 wt%, based on the total weight of the fraction. The Bio-carbon content in the stripped TLP fraction boiling above 370°C was about 0.35 wt%, based on the total weight of the fraction.

The results in the below tables show that the process according to the invention allows one to convert a biomass-derived pyrolysis oil in a safe and reliable manner through a hydrocracker to produce a Bio-carbon containing product that has comparable characteristics as a conventional hydrocracker product. This in turn advantageously allows one to substitute such conventional hydrocracker product with the Bio-carbon containing product without making any further changes to the product handling further downstream in the refinery.

Table 5: Yield Pattern of the Boiling Ranges of the Stripped TLP as Measured by SIMDIST (simulated distillation ASTM D7169).

TLP Boiling fraction	Arabian Medium Vacuum Residue only	Dewatered Hydrocarbon - Containing Mixture as Prepared in Example 1
Gasoline range: <210°C	7.5 %wt.	7.5 %wt.
Diesel range: 210-370°C	30 %wt.	30.5 %wt.
Vacuum Gas Oil range: 370-540 °C	33 %wt.	33.5 %wt.
Short Residue range: >540 °C	29.5 %wt.	28.5 %wt.
Total	100 %wt.	100 %wt.

5

Table 6: Component Distribution in the <370 °C Stripped TLP Boiling Fractions, as Determined by 2-Dimensional Gas Chromatography.

Components	Arabian Medium Vacuum Residue only	Dewatered Hydrocarbon-Containing Mixture as Prepared in Example 1
Paraffins	31.93 %wt.	31.34 %wt.
Naphtenes	18.36 %wt.	18.10 %wt.
di-Naphtenes	3.97 %wt.	4.16 %wt.
mono-Aromatics	16.28 %wt.	16.36 %wt.
Naphtenes-mono-Aromatics	13.40 %wt.	13.99 %wt.
di-Aromatics	7.23 %wt.	7.32 %wt.
Naphtenes-di-Aromatics	5.84 %wt.	5.95 %wt.
tri-Aromatics	2.33 %wt.	2.08 %wt.
>three Ring Aromatics	0.66 %wt.	0.69 %wt.

Table 7: Component Distribution in the 370°C - 470°C Stripped TLP Boiling Fractions, as Determined by 2-Dimensional Gas Chromatography.

Component	Arabian Medium Vacuum Residue only*	Dewatered Hydrocarbon-Containing Mixture as Prepared in Example 1
Paraffins	7.08	7.16
Naphtenes	4.59	4.55
di-Naphtenes	0.08	0.06
mono-Aromatics	6.00	6.08
Naphtenes-mono-Aromatics	1.71	1.90
di-Aromatics	1.75	1.87
Naphtenes-di-Aromatics	1.08	1.41
tri-Aromatics	2.44	2.64
>three Ring Aromatics	5.29	5.06

5

* based on a sample of stripped TLP obtained in period 3 as illustrated in table 4

Table 8, TLP Elemental Composition and Density.

	Period	STCA sample no.	C %wt.	H %wt.	N %wt.	S %wt.	O by dif. %wt.	H/C molar ratio	O/C Molar ratio times 100	Density kg/m ³ at 15 °C	MCRT %wt.
Arabian Medium Vacuum Residue only	1	12JPH00 2	87.2	11.5	0.278	0.732	0.29	1.58	0.25	931.1	6.0
Dewatered hydrocarbon-containing mixture as prepared in example 1	2	12JPH00 4	87	11.4	0.318	0.900	0.38	1.57	0.33	936.9	6.5
Arabian Medium Vacuum Residue only	3	12JPH00 6	87	11.3	0.339	1.105	0.26	1.56	0.22	941	7.5

Table 9, Elemental Composition and Density of < 370 °C Fraction.

	Period	STCA sample no.	C %wt.	H %wt.	N %wt.	S %wt.	O by dif. %wt.	H/C ratio molar	O/C ratio molar*100	Density kg/m ³ at 15 °C
Arabian Medium Vacuum Residue only	1	12JPH012	87	12.73	0.08	0.132	0.06	1.76	0.05	858.4
Dewatered hydrocarbon- containing mixture as prepared in example 1	2	12JPH014	87	12.72	0.098	0.156	0.03	1.75	0.02	857.7
Arabian Medium Vacuum Residue only	3	12JPH016	86.9	12.72	0.109	0.221	0.05	1.76	0.04	857.6

Table 10, Elemental Composition of > 370 °C Fraction.

	Period	STCA sample no.	C %wt.	H %wt.	N %wt.	S %wt.	O by dif. %wt.	H/C ratio molar	O/C ratio molar*100
Arabian Medium Vacuum Residue only	1	12JPH013	87.3	10.8	0.393	1.015	0.49	1.48	0.42
Dewatered hydrocarbon- containing mixture as prepared in example 1	2	12JPH015	87.0	10.6	0.444	1.200	0.71	1.47	0.61
Arabian Medium Vacuum Residue only	3	12JPH017	87.1	10.5	0.463	1.604	0.34	1.45	0.30

C L A I M S

1. A process for converting a biomass material comprising
a) pyrolyzing a biomass material to produce a biomass-derived
5 pyrolysis product;
b) mixing at least part of the biomass-derived pyrolysis
product and a petroleum-derived hydrocarbon composition,
which petroleum derived hydrocarbon composition has a C7-
asphaltenes content of equal to or more than 0.2 wt%, based
10 on the total weight of the petroleum-derived hydrocarbon
composition, to produce a hydrocarbon-containing mixture;
c) dewatering the hydrocarbon-containing mixture to produce a
dewatered hydrocarbon-containing mixture;
d) contacting the dewatered hydrocarbon-containing mixture
15 with hydrogen in one or more ebullating bed reactors
comprising a catalyst at a temperature in the range from 350
to 500°C to produce a reaction product.
2. The process according to claim 1, wherein the biomass
material is lignocellulosic material.
- 20 3. The process according to claim 2, wherein the
lignocellulosic material is washed, steam exploded, dried,
roasted, torrefied and/or reduced in particle size before
being pyrolyzed in step a).
3. The process according to claim 2 or 3, wherein step a)
25 further comprises the removal of minerals from the biomass
material before pyrolyzing and/or the removal of minerals
from the biomass-derived pyrolysis product or part thereof
after pyrolyzing.
4. The process according to anyone of the preceding claims,
30 wherein step a) is carried out in a pyrolysis reactor wherein
the biomass material is conveyed by means of a screw.
5. The process according to anyone of the preceding claims,
wherein in step a) a biomass-derived pyrolysis oil is
separated from the biomass-derived pyrolysis product and

wherein this biomass-derived pyrolysis oil is mixed with the petroleum-derived hydrocarbon composition in step b).

6. The process according to anyone of the preceding claims, wherein the petroleum-derived hydrocarbon composition in step
5 b) comprises a vacuum gas oil (VGO), a heavy coker gas oil, an atmospheric residue ("long residue"), a vacuum residue ("short residue") and/or mixtures thereof.

7. The process according to anyone of the preceding claims, wherein the biomass-derived pyrolysis product or part thereof
10 and the petroleum-derived hydrocarbon composition are mixed in step b) in a weight ratio of pyrolysis product to petroleum-derived hydrocarbon composition in the range from 10:90 to 20:80.

8. The process according to anyone of the preceding claims,
15 wherein in step c) the hydrocarbon-containing mixture is dewatered by means of evaporation.

9. The process according to claim 8, wherein such evaporation is carried out by flashing.

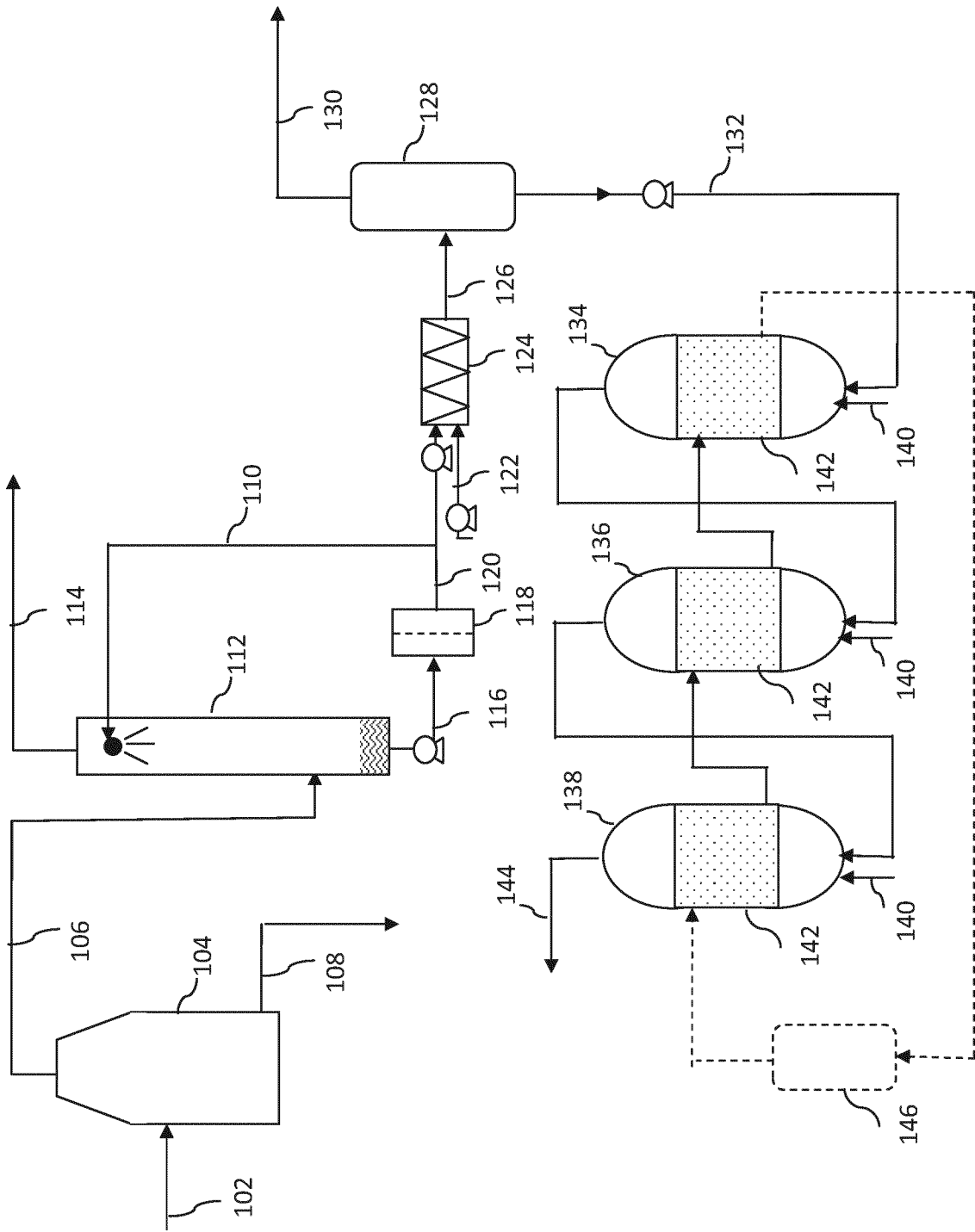
10. The process according to anyone of the preceding claims,
20 wherein the catalyst in step d) comprises a metal chosen from the group consisting of Molybdenum, Nickel, Copper, Tungsten, Cobalt, Palladium, Platinum, Ruthenium.

11. The process according to anyone of the preceding claims, wherein the catalyst in step d) comprises a heterogeneous
25 catalyst and/or a dispersed catalyst.

12. The process according to anyone of the preceding claims, wherein d) comprises supplying a feed comprising the dewatered hydrocarbon-containing mixture together with one or more co-feeds to the one or more ebullating bed reactors
30 and/or contacting the dewatered hydrocarbon-containing mixture with the catalyst in the presence of such one or more co-feeds.

13. The process according to claim 12, wherein the co-feed comprises petroleum-derived hydrocarbon composition and/or a lignocellulosic material and/or a cellulosic material.
14. The process according to anyone of the preceding claims,
5 wherein instead of or in addition to one or more ebullating bed reactors also one or more moving bed reactors and/or one or more slurry reactors are used.
15. The process according to anyone of the preceding claims, wherein the reaction product in step d) comprises one or more
10 cracked products.
16. The process according to anyone of the preceding claims, wherein the reaction product obtained in step d) is subsequently fractionated to produce one or more product fractions.
- 15 17. The process according to claim 16, wherein the one or more product fractions are blended with one or more additional components to produce a biofuel and/or biochemical, optionally after being hydrotreated and/or hydroisomerized.

Figure 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/058943

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C10B53/02 C10G47/26 C10G47/00 C10G33/00 C10G1/00
 C10G7/04 C10L1/04
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C10G C10B C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 2009/146225 A1 (UOP LLC [US]; BAUER LORENZ J [US]; MCCALL MICHAEL J [US]; BOLDINGH EDW) 3 December 2009 (2009-12-03) paragraph [0015] paragraphs [0005], [0011], [0012] page 12, lines 4-6, paragraph [0033] paragraphs [0028] - [0035] figure 1	1-17
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 15 July 2014	Date of mailing of the international search report 23/07/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Vaz, Miguel
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/058943

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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